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Oxygen isotopic measurements on the Cameca Nanosims 50

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Abstract

The Cameca Nanosims 50 has been designed to provide for parallel detection along a focal plane over a large mass range but spacing between adjacent mass lines makes it necessary to use miniature electron multipliers (EMs). A new version of a miniature EM, designed to reduce aging effects, has been tested. Means to characterize aging effects are presented. Data are interpreted by simulations with a simple model. Consequences of aging on isotopic measurements in a parallel detection context are examined in the special case of oxygen. Measurements of the most abundant isotope with a Faraday cup (FC) and weak isotopes with EMs are reported. Advantages of FC are emphasized: no dead time correction and no quasi-simultaneous arrivals to account for in a situation where high collection efficiencies (8% for O^- for instance) leads to large corrections.

Keywords: SIMS; Isotopes; Electron multiplier; Oxygen; Silicon

1. Introduction

The Nanosims 50 has been developed from the original design presented in SIMS VII [1,2]. The mass spectrometer achieves double focusing and high mass resolution at all positions along the focal plane. It includes seven detectors: four movable miniature electron multipliers (EMs), two EMs at fixed positions and one moveable Faraday cup (FC). The mass dispersion is large enough to allow simultaneous detection of ^{12}C, ^{13}C, ^{28}Si, ^{29}Si and ^{30}Si [3].

Detection of weak ion signals is conveniently made in the counting mode with EMs. However, EMs suffer from aging effects that cause the detection quantum efficiencies (DQEs) to decrease. Indeed, as counting proceeds, the mean heights of the electronic pulses coming out are progressively reduced so that pulse-height distributions (PHDs) appear more compressed. Because the discriminator threshold being set at a fixed value, fewer ions are counted for the same incoming ion flux inducing a decrease of DQE. On the average, the decrease of DQE depends upon the ion dose being received so that, after a certain operation time, DQEs of each EM are significantly different. In that respect, oxygen isotopic ratios deserve special attention because of the great abundance difference between ^{16}O and the two other isotopes ^{17}O and ^{18}O.

It is worth recalling that isotopic EM discriminations exist also in a sequential acquisition mode when three isotopes are successively addressed on the same EM. They occur because DQEs depend on isotopic masses and yield discriminations varying linearly with isotopic mass differences [4]. The aging effect is produced by the abundant isotope but all isotopes will

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suffer the same reduction of DQE, at least in a fist approximation. By comparison, in a parallel acquisition mode, the DQE of ^{16}O will decrease whereas DQEs of ^{17}O and ^{18}O will remain nearly constant resulting in a non-linear isotopic fractionation. Variations of isotopic discriminations due to aging still exist in the sequential mode but they represent a differential effect because the DQE reductions for ^{16}O, ^{17}O and ^{18}O due to aging are not exactly the same.

2. Characterization of aging effects

Two different types of miniature EM have been tested. Let us recall that those special EMs have been designed, for the NS50 mass spectrometer, to allow simultaneous detection of adjacent mass lines up to silicon [3]. Compared to conventional EMs the overall dimensions are reduced especially their width, which is less than 7 mm. On the first version (small), the other dimension were: 35 mm × 30 mm. In the second version (large), the width is kept at the same value but length and height are increased to 60 and 65 mm, respectively. Two methods of measurements have been used to characterize the aging effect: (i) change of the PHD shape and (ii) isotopic ratios reflecting DQE changes.

The first method records the change in the PHD shape as a function of the exposure time to a given ion flux. Two parameters have been selected, the pulse-height Max_D at which a PHD exhibits its maximum and the ratio D/G where D and G are the pulse-heights on the right and on the left side of the PHD maximum corresponding to the half maximum height of the PHD. The evolution recorded in Fig. 1a can be expressed by

$$\mathrm{Max}_D \propto \exp\left(-\frac{t}{\tau_D}\right) \quad (1)$$

where t is the exposure time and τ_D a fitting parameter (both expressed in mn).

It is known that the first dynode wearing may decrease the conversion yield N_p and induce a proportional shift of the PHD maximum Max_D. It also changes the PHD's shapes, which is reflected by changes in D/G ratios. Those behaviors can be observed in Fig. 1a and b where $\mathrm{Ln}(\mathrm{Max}_D)$ and D/G ratios are plotted for $^{32}S^-$ ions and increasing exposure times. In fact, the situation is a little more complicated because aging is not limited to a simple N_p decrease, it may also be caused by changes in electron–electron yields N_e of the other dynodes.

Simulations with a simplified model can provide us with an approximate evaluation of the general trends [4]. For instance in the reported case at $t = 0$ mn, with $N_\mathrm{p} = 11$ and $N_\mathrm{e} = 3$, calculations give a D/G ratio

Table 1
Comparison between calculated and experimental D/G ratios

Time (mn)	N_p	N_e low rank	N_e high rank	D/G calculated	D/G measured
0	11	3	3	2.64	2.64
180	7.3	3	3	3.58	3.16
180	8.45	3	2.91	3.16	3.16

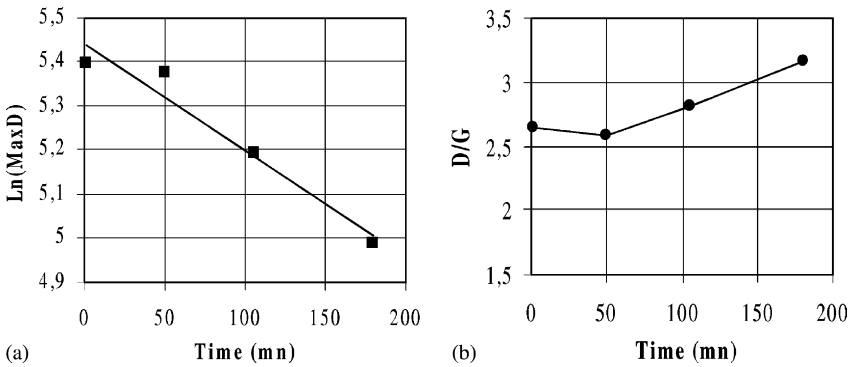

Fig. 1. (a) Evolution of $\mathrm{Ln}(\mathrm{Max}_D)$ for a $^{32}S^-$ ion flux of 1.4×10^6 cps over 3 h, Max_D has decreased by more than 34%. (b) Evolution of D/G during the same period.

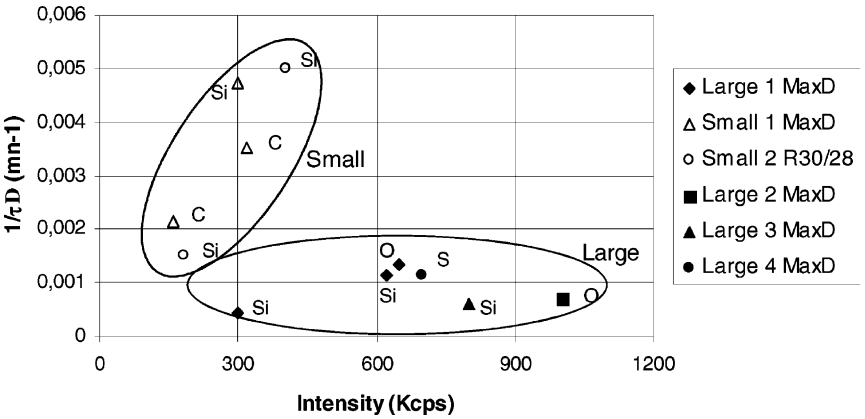

Fig. 2. Comparison between two EMs of first type (small) and four EMs of second version (large). For the second small EM (Small 2 R30/28), isotopic ratio $^{30}Si/^{28}Si$ has been recorded to determine $1/\tau_D$, while the Max_D method has been used for the five others. Four different species of secondary ions have been tested: $^{12}C^-$, $^{16}O^-$, $^{28}Si^-$ and $^{32}S^-$.

equal to 2.64. If, after 180 mn exposure time, the shift of the maximum was entirely due to the decrease of N_p, the new N_p should be equal to 7.31. But then, the ratio calculated for D/G would be 3.58, whereas the experimental value is about 3.16 (Table 1). Thus, it appears clearly that the decrease of the total gain of the EM must be also due to changes of N_e in the other dynodes.

Since the decline of N_e is mainly due to hydrocarbon contamination stimulated by electron bombardment [5] and since higher electron fluxes are found on higher rank dynodes, it seems reasonable, in a first approximation, to assume that N_e stay the same for the first ranks. Then, it is possible to account for $D/G = 3.16$ by taking $N_e = 3$, as before, and $N_p = 8.45$ but now we have to assume that there is an additional decrease of the gain. If the latter was uniformly shared by the last five dynodes, the relative decrease of N_e would only be about 3% for each of those dynodes.

It should be emphasized that evolutions with exposure times depend upon the whole history of the EM and may also be different from one EM to the other. For instance, the pulse height at the distribution maximum may change while the ratio D/G remains nearly constant over a given period of time, demonstrating that in such a case the deterioration of the higher rank dynode yields are the main cause for EM aging.

The second method records the evolution of DQE with the exposure time. The most abundant isotope and a weak one are recorded in parallel with two different EMs. The EM receiving the abundant isotope exhibits a change of its DQE while the other EM that can be assumed to have a DQE nearly constant during the measurement. The ratio R of the two isotopes varies with the exposure time and its evolution depends upon the decline of the DQE of the EM receiving the abundant isotope, which can be represented by an expression similar to (1). By comparing aging effects on PHDs and on isotopic ratios, it has been determined experimentally that the parameters τ_R and τ_D are related by relation (2) approximately (Fig. 2):

$$\frac{1}{\tau_D} \cong 20\left(\frac{1}{\tau_R}\right) \tag{2}$$

For both versions of EM, aging effect seems to be insensitive to the ion monoatomic species being used but proportional to ion dose. Aging effect are reduced on the second version of EM (large) by a factor ranging from 5 to 22 depending of the EM! The large version, now installed on the Nanosims 50, has been used for the following measurements.

3. Oxygen isotopic ratios with EM and FC

An obvious consequence of the previous data is that the most abundant isotopes should be measured with an FC while the weaker isotopes are measured with

Table 2
Aging effect on oxygen isotopic ratios

Ratio	Before (t_1)	$\sigma_R/\bar{R}$ (‰)	After (t_2)	$\sigma_R/\bar{R}$ (‰)	$\Delta R/R$ (‰)
$^{17}O/^{16}O$ (10^{-3})	0.37379	0.56	0.36915	1.7	−12.4
$^{18}O/^{16}O$ (10^{-3})	1.85850	1.60	1.86490	0.67	3.4
$^{18}O/^{17}O$	4.973	1.20	5.054	1.99	16.3

EMs. In the following set of experiments on oxygen isotopic ratios measurements, ^{16}O has been measured with FC while ^{17}O and ^{18}O have been detected on two different EMs.

A new thermo-regulated electronic system based on a dedicated Finigan Mat preamplifier ($R = 10^{11}$ Ω) has been designed. This preamplifier is connected to a voltage/frequency converter leading to a conversion factor: 1 pA = 10^4 Hz. The noise defined as the standard deviation of the offset over an integration time of 5 s is 3×10^{-16} A.

The consequence of aging on isotopic ratio measurements with EMs and the advantage of using an FC for the most abundant isotope can be illustrated by the example summarized in Table 2. Measurements of $^{17}O/^{16}O$, $^{18}O/^{16}O$ and $^{18}O/^{17}O$ are made in parallel over a period of time Δt starting at $t = t_1$ with ^{16}O being addressed in the FC, ^{17}O in EM1 and ^{18}O in EM2. Then ^{16}O is addressed in EM1 for a period of time long enough to produce a sizable aging effect. The isotopic measurements are resumed at time t_2, $(t_2 - t_1) \gg \Delta t$, using the same scheme as previously, it means that ^{17}O is now measured with EM1, which has been purposely aged by its long exposure to ^{16}O. Relative differences $\Delta R/R = [R(t_2) - R(t_1)]/R(t_1)$ for the ratios $^{17}O/^{16}O$ and $^{18}O/^{17}O$ are respectively about −1.4 and 1.4% whereas $^{18}O/^{16}O$ stays nearly the same. It shows clearly that the DQE of EM1 decreased during the exposure to ^{16}O and that the DQE of EM2 remained the same. In addition, it can be observed that the relative variation of the maximum positions, $[\mathrm{Max}(t_2) - \mathrm{Max}(t_1)]/\mathrm{Max}(t_1)$, is about 25%. According to (2), the associated relative variation of DQE is expected to range between 1.25%, in reasonable agreement with the observed effects.

4. Conclusions

The new EM design has reduced the aging effect by roughly 1 order of magnitude. For precise isotopic ratios measurements, when the most abundant isotope is approximately 20 times above the others, it is advisable to use an FC. There are other substantial advantages in doing so: no dead time correction, no quasi-simultaneous arrival correction (QSA) (which will be particularly important here because of the high collection efficiency [4]). In addition, since the intensity of the most abundant isotope can be brought above 10^6 cps, limit beyond which precise dead time corrections become hazardous, higher primary ion currents can be used to increase the count rates on weak isotopes and speed up acquisition times.

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